Class - B.Sc. Part - III
subject - chemistry (organic)
Paper - VII
Topic - Knoevenagel reaction

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Knoevenagel reaction

condensation reaction of compound having active methylene group with carbonyl compound (an aldehyde or ketone) is known as Knoevenagel reaction. This reaction is catalysed by ammonia or its derivative i.e. 1°, 2° or 3° amines leading to the formation of unsaturated compounds.

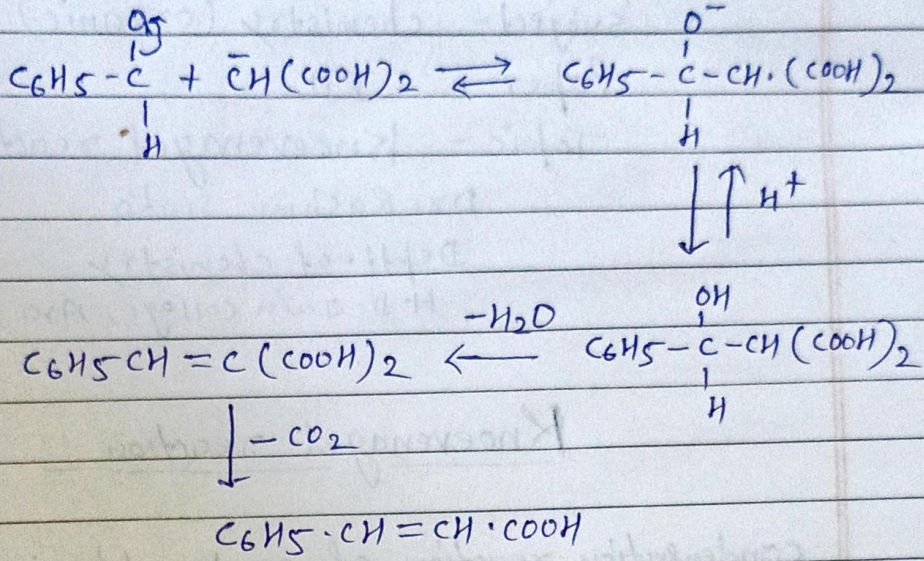
$$C_6H_5\text{-}CHO + H_2C(COOH)_2 \longrightarrow C_6H_5\text{-}CH=C(COOH)_2 \xrightarrow{-CO_2} C_6H_5\text{-}CH=CH\cdot COOH$$

The compounds with active methylene groups may be acid, ester, nitrile or nitroparaffin.

Mechanism :- The stepwise mechanism of this reaction is as follows :-

The base removes a proton from the active methylene group to form carbanion which then adds on the carbonyl gr. of the aldehyde to form an adduct which on dehydration followed by the decarboxylation gives an α-β-unsaturated

dibasic acid.



Knoevenagel reaction is more useful with aromatic than with aliphatic aldehydes, since the product with the latter further undergoes Michael reaction. e.g. –

$$CH_3CHO + CH_2(COOC_2H_5)_2 \longrightarrow CH_3CH=C(COOC_2H_5)_2$$

$$\xrightarrow[\text{Michael reaction}]{CH_2(COOC_2H_5)_2} CH_3CH\begin{cases} CH(COOC_2H_5)_2 \\ CH(COOC_2H_5)_2 \end{cases}$$

So, the net reaction with aliphatic aldehydes may be summed up as below :–

$$RCHO + 2CH_2(COOC_2H_5)_2 \longrightarrow RCH\begin{cases} CH(COOC_2H_5)_2 \\ CH(COOC_2H_5)_2 \end{cases}$$

Furthermore, Ketones also do not undergo Knoevenagel reaction with malonic acid or its esters but can do so with more active

cyanoacetic acid and its esters. e.g. –

$$(CH_3)_2C=O + H_2C\begin{cases} CN \\ COOC_2H_5 \end{cases} \xrightarrow[-H_2O]{CH_3CONH_2,\ CH_3COOH}$$

$$(CH_3)_2C=C\begin{cases} CN \\ COOC_2H_5 \end{cases} \xrightarrow{H_2O} (CH_3)_2C=CHCOOH$$

The Knoevenagel reaction is reversible and under ordinary conditions the equilibrium lies to the left with the result the yeild of the product is usually not satisfactory. However, cope introduced an improved procedure by carrying out the reaction in benzene and removing the water formed, as an azeotropic mixture in the Dean and Stark apparatus and thus shifting the equilibrium completely to the right. Such type of Knoevenagel reaction is therefore known as cope-Knoevenagel reaction